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13. ABSTRACT (Maximum 200 words)

The goal of this research is to improve basic understanding of how thermodynamics and nucleation kinetics influence the deposit of pyrolytic products from supercritical fuels. The precipitation of picene from supercritical methylcyclohexane was investigated theoretically, under the assumptions of both thermodynamic and kinetic control. The kinetic calculations indicated that a negligible amount of deposits were formed as a result of friction-driven depressurization in tubular flow. However, the presence of small amounts of particulate impurities dramatically enhanced the rate of deposit formation. For isobaric cooling conditions, the rate of deposit formation was found to depend sensitively on whether the mixture entered the retrograde region or not. In the retrograde region where solubility decreases with increasing temperature, isobaric cooling was found to suppress deposit formation. The time evolution of isolated quiescent droplets exposed to an excess of partially miscible compressed solvent was investigated under sub-critical conditions. Over a wide range of conditions the calculations showed appreciable droplet swelling, followed by evaporation. An aerosol dynamics code was combined with mass, momentum, energy balances and equation of state calculations to yield the evolution of the particle size during steady, one-dimensional friction-driven expansions of a supercritical fluid containing a dissolved solute.

14. SUBJECT TERMS Homogeneous and hetergeneous nucleation; supercritical fuels; deposit formation			**15. NUMBER OF PAGES** 8
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THEORETICAL AND COMPUTATIONAL STUDIES OF NUCLEATION IN SUPERCRITICAL FUELS

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SUMMARY/OVERVIEW

The objective of this research is to improve the basic understanding of how thermodynamics and nucleation kinetics influence the deposit of pyrolytic products from supercritical fuels. We investigate the precipitation of picene from supercritical methylcyclohexane under both thermodynamic and kinetic control. The kinetic calculations are useful for identifying operating conditions that minimize deposit formation. We also model the time evolution of single organic droplets exposed to an excess of miscible supercritical fluid, the typical configuration used in the supercritical anti-solvent (SAS) process for the production of microparticulate polymeric powders. Finally, we compute the particle size distribution during the adiabatic expansion of a supercritical fluid containing dissolved solutes, accounting for nucleation, condensation, and coagulation.

TECHNICAL DISCUSSION

The Statistical Associating Fluid Theory (SAFT) was used to model the fluid-phase equilibrium of picene in methylcyclohexane (Huang and Radosz, 1990). An expression based on classical nucleation theory with due account for fluid-phase nonideality was used to calculate the deposition rate of picene from methylcyclohexane (Debenedetti, 1990). Steady, one-dimensional, friction-driven, adiabatic expansions were described by coupling mass, momentum, and energy balances with the SAFT equation of state (Lele and Shine, 1992).

Figures 1 and 2 contrast predictions for thermodynamically and kinetically-controlled precipitation of picene from supercritical methylcyclohexane solutions during partial adiabatic expansion while flowing through cylindrical tubes. Figure 1 illustrates the effects of varying inlet temperature and pressure of methylcyclohexane solutions. The assumption of instantaneous precipitation (thermodynamic control) always leads to substantial accumulation of solid-phase picene. The kinetic calculation, however, suggests that to minimize deposits along fuel transfer lines it is advantageous to operate with low inlet temperatures and high inlet pressures. Figure 2 depicts the effects of varying inlet pressure and transfer line length. Longer transfer lines give rise to larger fuel expansions,

which result in greater solute precipitation. Results which account for nucleation kinetics indicate that there exists a critical length for each inlet pressure above which deposit formation occurs suddenly and rapidly approaches the limit of instantaneous precipitation. Higher inlet pressures enable longer transfer lines before the burst of nucleation occurs.

The supercritical antisolvent (SAS) process has been used in several experimental studies for the precipitation of polymers with interesting morphologies (Yeo *et al.*, 1993) and biologically active protein particles (Winters *et al.*, 1996). However, the complex interaction of jet hydrodynamics, phase behavior, and mass transfer that governs the process has not been investigated theoretically. Theoretical work on fuel droplet combustion (Hsieh *et al.*, 1991; Jia and Gogos, 1993) was used as a basis for developing a model which predicts the evolution in time of a single droplet of an organic solvent exposed to an excess of miscible supercritical fluid. Mass transfer occurs in two directions: from the solvent droplet into the supercritical fluid and from the supercritical fluid into the droplet.

Figure 3A shows the effect of pressure on the initial interfacial molar flux for several isotherms. The temperatures and pressures shown are typical for SAS operation. It can be seen that the initial molar flux is always into the droplet. Each isotherm passes through a minimum, which corresponds to the pressure for maximum droplet swelling. The sensitivity to pressure is greater near the critical temperature of the supercritical fluid. Figure 3B shows the change in the droplet radius as a function of time. Droplet lifetimes are characterized by rapid diffusion of supercritical fluid into the droplet, followed by gradual shrinking as the organic solvent diffuses into the excess supercritical fluid. These results suggest that the model can be used to gain insight into the relationship between operating conditions (temperature, pressure, droplet size) and droplet behavior as a function of time.

We have developed an aerosol dynamics code that tracks the evolution of the particle size distribution during steady, one-dimensional expansion of a supercritical fluid containing dissolved solutes. The calculation takes into account fluid-phase nonideality, nucleation, condensation, and inter-particle coagulation. Figure 4 shows the evolution of the particle size distribution during a friction-driven adiabatic expansion. This is the first time that this type of calculation has been implemented to study particle formation in supercritical fluids.

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Winters, M. A., Knutson, B. L., Debenedetti, P. G., Sparks, H. G., Przybycien, T. M., Stevenson, C. L., Prestrelski, S. J. 1996. J. Pharm. Sci. **85:** 586.
Yeo, S. D., Debenedetti, P. G., Radosz, M., Schmidt, H. W. 1993. Macromolecules. **26:** 6207.
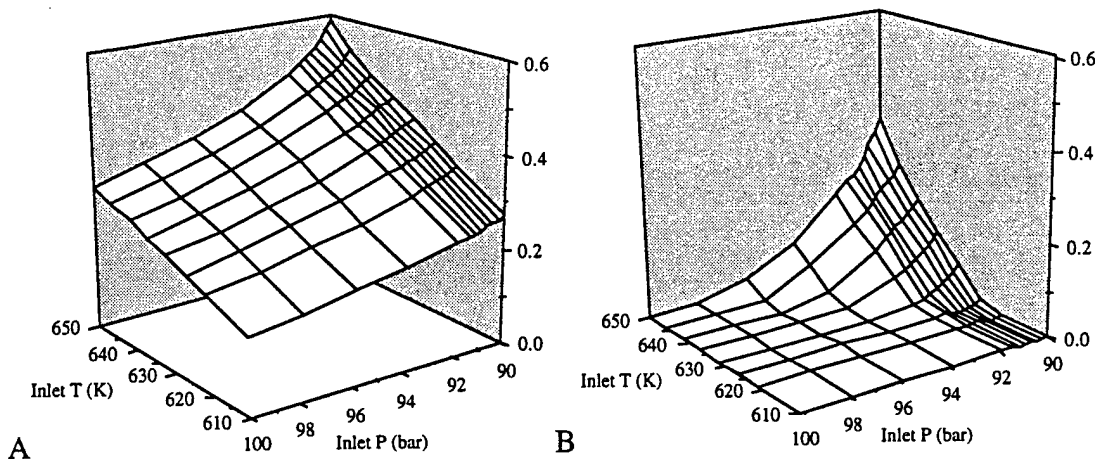
Figure 1: (A) Instantaneous and (B) kinetically-constrained precipitation of picene from adiabatically-expanding supercritical methylcyclohexane flowing through a cylindrical tube [length (L) = 0.40 m, diameter (D) = 2.0 mm]. The vertical axis gives the cumulative amount precipitated as a fraction of the total inlet flow. The assumption of instantaneous precipitation always leads to a substantial accumulation of solid-phase picene. The more realistic, kinetically-controlled calculations show that it is possible to suppress precipitation by operating at low enough inlet temperatures and high enough inlet pressures.
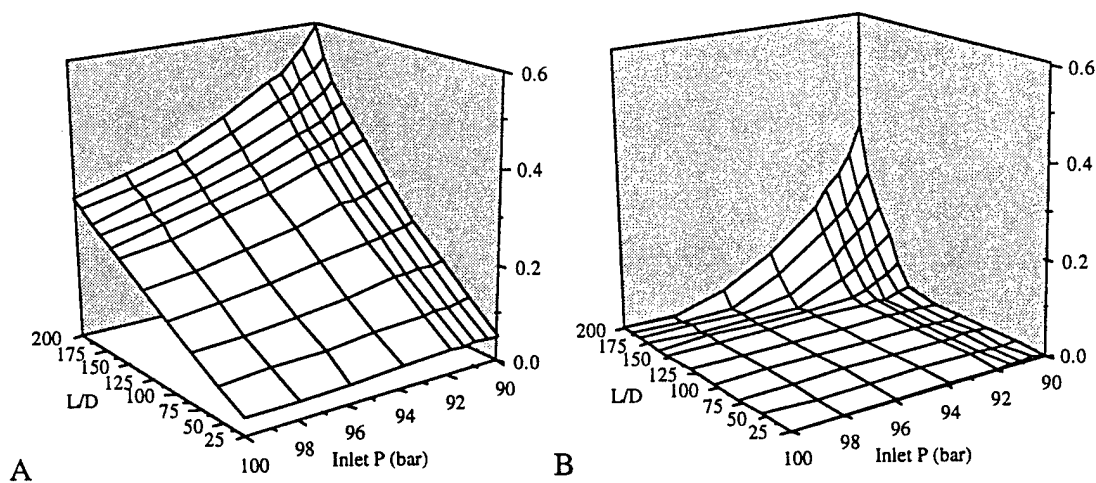

Figure 2: (A) Instantaneous and (B) kinetically-constrained precipitation of picene from adiabatically-expanding supercritical methylcyclohexane flowing through a cylindrical tubing [length (L) = 0.05 to 0.40 m, diameter (D) = 2.0 mm]. Same vertical scale as in Figure 1. Inlet temperature maintained at 650 K. There is a critical length for each inlet pressure at which accumulation rapidly increases, approaching the limit of instantaneous precipitation.
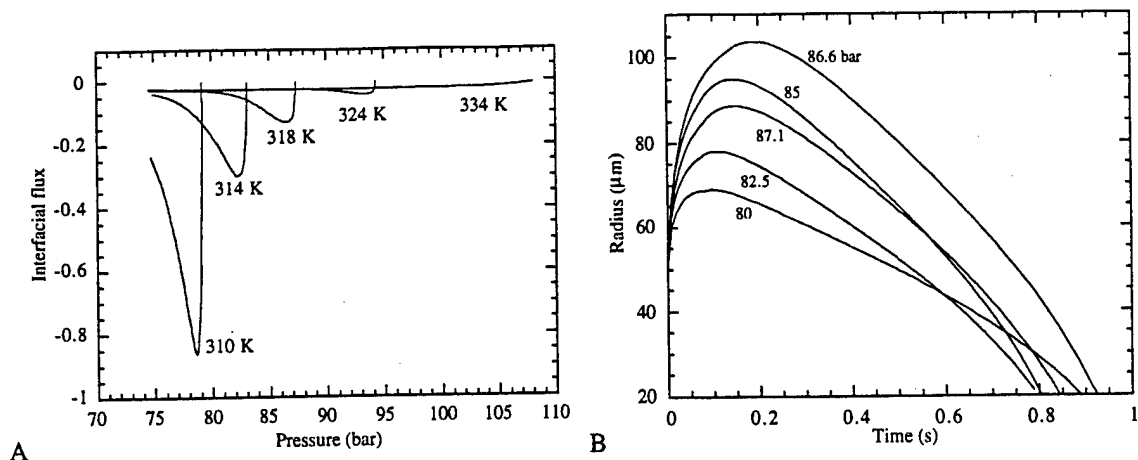
Figure 3: (A) Effect of temperature and pressure on the initial interfacial molar flux for toluene droplets exposed to an excess of supercritical carbon dioxide. Negative values indicate net flux into droplet. The molar flux has been scaled with $[4000 \cdot \rho^* \cdot D^*/r_o]$ where ρ^* and D^* are, respectively, the saturated molar density and diffusivity of the liquid phase, and r_o is the initial droplet radius. (B) Evolution of toluene droplet radius at 318 K and different carbon dioxide pressures.
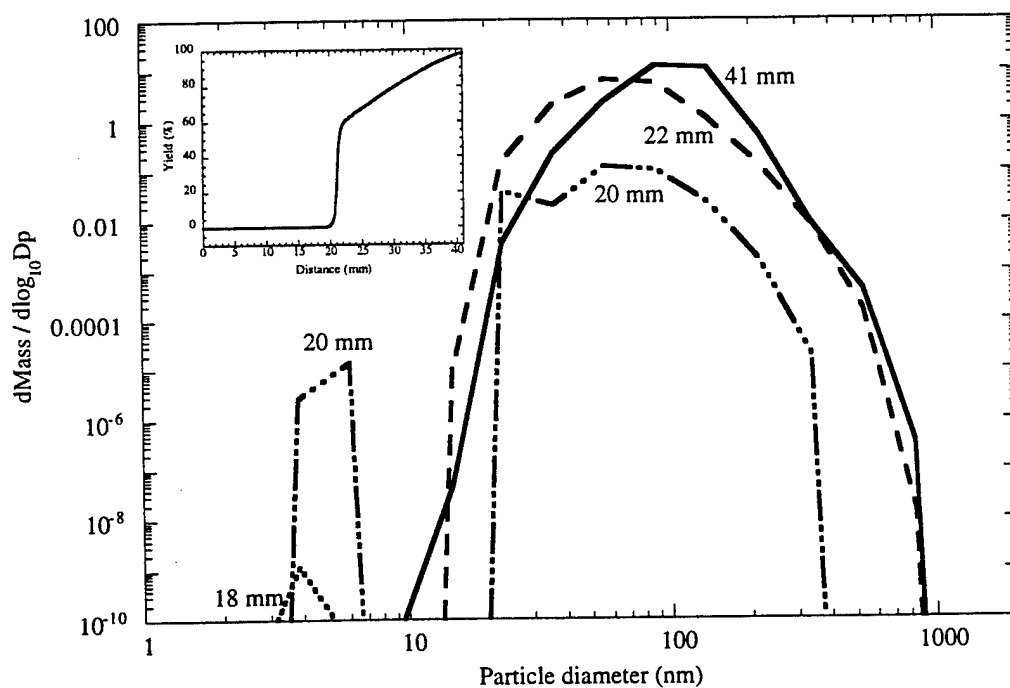

Figure 4: Evolution of the particle size distribution for phenanthrene precipitating from supercritical carbon dioxide expanding in a (50 micron x 41 mm) capillary. Inlet conditions: 200 bar and 325K. The inset shows the total precipitated mass, expressed as a percentage of the total amount of solute present initially, along the capillary's axis.

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3. PERSONNEL SUPPORTED

Michael Winters; graduate student

Pablo G. Debenedetti; principal investigator

4. PUBLICATIONS

M.A. Winters, D.Z. Frankel, P.G. Debenedetti, J. Carey, M. Devaney, and T.M. Przybycien, "Protein Purification with Vapor-Phase Carbon Dioxide." **Biotech. & Bioeng.**, in press, (1998).

5. PRESENTATIONS

"Materials Processing with Supercritical Fluids." Engineering Foundation Conference on Separation Technology: Separations for Clean Production. Davos, Switzerland, October 28, 1997.

"Phase Separation by Nucleation and Growth, and by Sipnodal Decomposition: Fundamentals." II NATO Advanced Study Institute on Supercritical Fluids. Kemer, Turkey, July 20, 1998.

6. HONORS/AWARDS

Presidential Young Investigator, NSF, 1987
Camille and Henry Dreyfus Teacher-Scholar, Dreyfus Foundation, 1989
John Simon Guggenheim Memorial Foundation Fellowship, 1991
Best Professional Book in Chemistry to *Metastable Liquids*, Assoc.Amer.Pubs., 1996
Professional Progress Award, American Institute of Chemical Engineers, 1997

Principal Investigator Annual Data Collection (PIADC) Survey Form

NOTE: If there is insufficient space on this survey to meet your data submissions, please submit additional data in the same form as identified below.

PI DATA

Name (Last, First, MI) ___Debenedetti, Pablo G.___

Institution ___Princeton University___

Contract/Grant No ___F49620 – 96 – 1 – 0169___

NUMBER OF CONTRACT/GRANT CO-INVESTIGATORS

Faculty __1__   Post Doctorates_____   Graduate Students __1__   Other_____

PUBLICATIONS RELATED TO AFOREMENTIONED CONTRACT/GRANT

NOTE List names in the following format: Last Name, First Name, MI

Include: Articles in peer reviewed publications, journals, book chapters, and editorships of books.

Do Not Include Unreviewed proceedings and reports, abstracts, "Scientific American" type articles, or articles that are not [ ] reports of new data, and articles submitted or accepted for publication, but with a publication date outside the stated time fra[ ]

Name of Journal, Book, etc ___Biotechnology and Bioengineering___

Title of Article ___Protein Purification with Vapor-Phase Carbon Dioxide___

Author(s) ___Winters, M.A.; Frankel, D.Z.; Debenedetti, P.G.; Carey, J.; Devaney, M.; Przybycien, T.M.___

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Author(s) _____

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HONORS/AWARDS RECEIVED DURING CONTRACT/GRANT LIFETIME

Include: All honors and awards received during the lifetime of the contract or grant, and any life achievement honors such as (Nobel prize, honorary doctorates, and society fellowships) prior to this contract or grant.

Do Not Include: Honors and awards unrelated to the scientific field covered by the contract/grant.

Honor/Awards: Professional Progress Award   Year Received: 1997

Honor/Award Recipient(s): Pablo G. Debenedetti

Awarding Organization: American Institute of Chemical Engineers

Honor/Awards: Best Professional/Scholarly Book in
             Chemistry "Metastable Liquids"   Year Received: 1996

Honor/Award Recipient(s): Princeton University Press

Awarding Organization: Association of American Publishers, Inc.

Honor/Awards: Guggenheim Fellow   Year Received: 1991

Honor/Award Recipient(s): Pablo G. Debenedetti

Awarding Organization: John Simon Guggenheim Memorial Foundation

Honor/Awards: Camille & Henry Dreyfus Teacher-Scholar   Year Received: 1989

Honor/Award Recipient(s): Pablo G. Debenedetti

Awarding Organization: Camille & Henry Dreyfus Foundation

Honor/Awards: Presidential Young Investigator   Year Received: 1987

Honor/Award Recipient(s): Pablo G. Debenedetti

Awarding Organization: National Science Foundation